

# 3  
PATENT

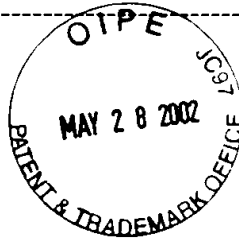
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:  
Stamires, Dennis, et al.

Serial No.: 10/066,079  
Filing Date: January 31, 2002

For: QUASI-CRYSTALLINE CARBOXYLATES

Assistant Commissioner for Patents  
Washington, D.C. 20231



Docket: ACH2850US

Examiner:

Group Art Unit: 1754

CERTIFICATE OF MAILING  
I hereby certify that this correspondence is being  
deposited with the United States Postal Service  
as First-Class mail in an envelope addressed to:  
Assistant Commissioner for Patents  
Washington, DC 20231

on May 13, 2002  
Angelique Anderson  
Angelique Anderson

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Sir:

Enclosed herewith is a certified copy of European Patent Application No.  
01200833.0, filed March 5, 2001 in connection with the above-identified application.

Respectfully submitted,

Louis A. Morris  
Louis A. Morris  
Attorney for Applicant(s)  
Reg. No. 28,100

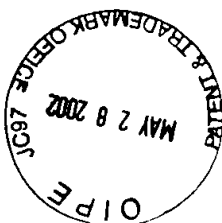
Akzo Nobel Inc.  
Intellectual Property Department  
7 Livingstone Avenue  
Dobbs Ferry, N.Y. 10522  
(312) 906-7769



Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

01200833.0

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

R C van Dijk

DEN HAAG, DEN  
THE HAGUE, 01/02/02  
LA HAYE, LE



**Blatt 2 der Bescheinigung**  
**Sheet 2 of the certificate**  
**Page 2 de l'attestation**

Anmeldung Nr.:  
Application no.:  
Demande n°: 01200833.0

Anmeldetag:  
Date of filing:  
Date de dépôt: 05/03/01

Anmelder:  
Applicant(s):  
Demandeur(s):  
Akzo Nobel N.V.  
6824 BM Arnhem  
NETHERLANDS

Bezeichnung der Erfindung:  
Title of the invention:  
Titre de l'invention:

Quasi-crystalline hydrated magnesium aluminium hydroxy carboxylates, process for their preparation  
and the use thereof

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: US  
State:  
Pays:

Tag: 09/02/01  
Date:  
Date:

Aktenzeichen: USP 103676  
File no.  
Numéro de dépôt:

Internationale Patentklassifikation:  
International Patent classification:  
Classification internationale des brevets:

C07C51/41, C01F7/00, C01F7/16, C07C53/10, C07C53/06, B01J21/00, B01J31/04, B01J21/16

Am Anmeldetag benannte Vertragsstaaten:  
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR  
Etats contractants désignés lors du dépôt:

Bemerkungen:  
Remarks:  
Remarques:

See for original title of the application  
page 1 of the description.

## QUASI-CRYSTALLINE CARBOXYLATES

EPO - DG 1

05 03 2001

## FIELD OF THE INVENTION

(44)

- 5 The present invention relates to a composition comprising a quasi-crystalline hydrated magnesium-aluminium hydroxy carboxylate, its preparation and use. The invention also relates to the preparation of magnesium-aluminium solid solutions and anionic clays by using the carboxylate compositions as intermediate.

10

## BACKGROUND OF THE INVENTION

- One object of the present invention is a new process for the production of anionic clays. A variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydrotalcite-like and layered double hydroxide is interchangeably used by those skilled in the art. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

- 15 Anionic clays have many applications. These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular Van Broekhoven (US 4,956,581 and US 4,952,382) has described their use in SO<sub>x</sub> abatement chemistry.

25

The preparation of anionic clays has been described in many prior art publications. For work on anionic clays, reference is given to the following articles:

Helv. Chim. Acta, 25, 106-137 and 555-569 (1942)

- 30 J. Am. Ceram. Soc., 42, no. 3, 121 (1959)

Chemistry Letters (Japan), 843 (1973)

Clays and Clay Minerals, 23, 369 (1975)

Clays and Clay Minerals, 28, 50 (1980)

Clays and Clay Minerals, 34, 507 (1996)

Materials Chemistry and Physics, 14, 569 (1986).

In addition there is an extensive amount of patent literature on the use of  
5 anionic clays and processes for their preparation.

Two major reviews of anionic clay chemistry were published in which the  
synthesis methods available for anionic clay synthesis have been summarised:

F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and  
10 Applications," Catalysis Today, 11 (1991) Elsevier Science Publishers B. V.  
Amsterdam.

J P Besse and others "Anionic clays: trends in pillary chemistry, its synthesis  
and microporous solids"(1992), 2, 108, editors: M.I. Occelli, H.E. Robson, Van  
15 Nostrand Reinhold, N.Y.

Two types of anionic clay preparation are described in these reviews. The most  
conventional method is co-precipitation (in Besse this method is called the salt-  
base method) of a soluble divalent metal salt and a soluble trivalent metal salt  
under alkaline conditions, optionally followed by hydrothermal treatment or  
20 aging to increase the crystallite size. The second method is the salt-oxide  
method in which a divalent metal oxide is reacted at atmospheric pressure with  
a soluble trivalent metal salt, followed by aging under atmospheric pressure.  
This method has only been described for the use of ZnO and CuO in  
combination with soluble trivalent metal salts.

25 The prior art anionic clays are all prepared by reaction of a magnesium source  
and an aluminium source under basic conditions, most typically at pH values in  
the range 8-10 and above. The basic reaction environment, however, leads to  
corrosion of equipment and limits the processing conditions of their preparation  
30 and any subsequent reaction. It is therefore an object of this invention to  
prepare anionic clays in mildly acidic environment.

In the above mentioned reviews the authors state that a characteristic of anionic clays is that mild calcination at 500°C results in the formation of a disordered MgO-like product. Said disordered MgO-like product is distinguishable from spinel (which results upon severe calcination) and from anionic clays. In this specification we refer to said disordered MgO-like materials as Mg-Al solid solutions. In contrast to spinel, which is a stable, irreversible phase, these Mg-Al solid solutions contain a well-known memory effect whereby the exposure to water of such calcined materials results in the reformation of the anionic clay structure. These solid solutions are the active SO<sub>x</sub> adsorbers under FCC regenerator conditions. Like anionic clays, prior art Mg-Al solid solutions are prepared under basic conditions.

The production of spinel at acidic conditions is disclosed in EP 0-573 610. The disclosed process consists of rapidly drying an acidic slurry of a magnesium and an aluminium compound, followed by calcination. This process differs from the present invention in several ways. First, the products after calcination are different. The product of the present invention is a solid solution which can be rehydrated to an anionic clay; EP 0 573 610 produces spinels, which cannot be rehydrated to anionic clays. Secondly, the present invention is related to quasi-crystalline magnesium-aluminium carboxylates. These materials are not formed as intermediates in the process according to EP 0 573 610, because no aging step is performed. Aging is essential for the formation of QCCs according to the present invention.

25

## SUMMARY OF THE INVENTION

The present invention provides new compositions of matter, referred to as quasi-crystalline carboxylates (QCCs), their preparation and use. These materials comprise a quasi-crystalline hydrated magnesium-aluminium hydroxy carboxylate. These quasi-crystalline carboxylates are characterised by at least a strong reflection in the powder X-ray diffraction pattern at a basal spacing in the range of 5 to 15 Å. The QCCs according to the invention may optionally comprise a hydrated magnesium hydroxy carboxylate, a hydrated aluminium hydroxy carboxylate and/or aluminium oxide.

The invention further relates to a process for preparing QCCs, Mg-Al solid solutions and anionic clays under acidic conditions. The method comprises aging of an acidic mixture of a magnesium carboxylate and an aluminium source, resulting in a QCC. Calcination of this composition results in a Mg-Al solid solution; rehydration of this solid solution gives an anionic clay.

## DETAILED DESCRIPTION OF THE INVENTION

Carboxylate salts of electropositive metals such as magnesium can be readily prepared by reaction of the oxide with an aqueous solution of the free acid form of the desired carboxylate. Thus, magnesium acetate can be readily obtained simply by the reaction of magnesium oxide, i.e. magnesia, with a carboxylic acid in aqueous solution. Alternatively, magnesium hydroxide may be substituted for magnesium oxide as the source of magnesium in the above reaction.

Metal carboxylates are highly attractive as precursors of metal oxides. When these salts are heated in air to their decomposition temperature the primary products are the oxide of the metal, environmental benign carbon dioxide and water. Typical examples of hydroxides suitable for the formation of the quasi-crystalline magnesium-aluminium carboxylates according to the invention

include monocarboxylates, such as acetate, formate, propionate, and other carboxylates, and dicarboxylates, e.g. oxalate, malonate, succinate, etcetera. Particularly preferred carboxylates are acetate and formate. Formic acid is cheap and reacts readily with magnesium oxide to form magnesium formate, although its solubility and reactivity toward active aluminas is lower than that of acetate.

Both aluminium salts, aluminium hydroxides, aluminium oxides and mixtures thereof can be used as aluminium source for the preparation of the quasi-crystalline magnesium-aluminium carboxylates according to the present invention.

Aluminium salts include aluminium nitrate, aluminium chloride, aluminium carboxylates, and mixtures thereof. Preferred aluminium salts are aluminium nitrate and aluminium carboxylates. These nitrate and carboxylate anions will be destroyed upon calcination, making washing steps redundant.

Aluminium oxides, so-called aluminas, that can be used include amorphous forms of hydrous aluminium oxides, which are also known as active aluminas, transition aluminas, and mixtures thereof. Active aluminas, which include aluminium hydroxide gel powders, are commercially available reagents. A very important transition alumina is pseudo-boehmite. This is a commercially available hydrous alumina with an idealised composition of  $\text{AlO}(\text{OH})$ . Pseudo-boehmite exhibits a powder X-ray diffraction (PXRD) pattern with peaks at the positions found for boehmite, but owing to the presence of a small particle size and structural defects, the diffraction peaks are very broad. Pseudo-boehmites may or may not be peptisable in acidic solution. One commercially available pseudo-boehmite that is peptisable is produced by the Vista Chemical Company under the name Catapal A®. Non-peptisable pseudo-boehmites are supplied by the LaRoche Chemical Company, under the name Versal-250®, and Condea Chemie, under the name P-200®.

30



The aluminium source and the magnesium carboxylate are fed to a reactor and aged in aqueous suspension to obtain the quasi-crystalline carboxylate according to the invention. Within the context of this invention a reactor is considered to be any confined zone in which the reaction between the aluminium source and magnesium source takes place. The reactor may be  
5 equipped with stirrers, baffles etcetera to ensure homogeneous mixing of the reactants.

Said aqueous suspension in the reactor may be obtained by either adding slurries or solutions of the starting materials, either combined or separate, to the  
10 reactor or adding the magnesium carboxylate to a slurry of the aluminium source or vice versa and adding the resulting slurry to the reactor. It is possible to treat, for instance the aluminium source slurry at elevated temperature and then add either the magnesium carboxylate per se, or add the magnesium carboxylate in a solution either to the reactor or the aluminium slurry. Especially  
15 when using metal sources like oxides or hydroxides, it is usually advisable to mill the metal source before use. Preferably, both the aluminium source and the magnesium carboxylate are milled before use. When wet milling is used, the slurry containing both the aluminium source and the magnesium carboxylate may be wet milled, for instance in a ball mill.

20 The reaction takes place during aging. Within the context of this description aging means treatment at ambient or at elevated temperature and at atmospheric or elevated pressure for a time period in the range of 15 minutes to 60 hours. The aging time depends on the temperature and the activity of the  
25 starting materials. Usually, a temperature between room temperature and 300°C is used at or above atmospheric pressure. It is preferred to carry out the process at temperatures above 50°C rather than at room temperature, because this results in compositions with sharper peaks in the X-ray diffraction pattern than QCCs obtained at room temperature. The reactor may be heated by any  
30 heating source such as a furnace, microwave, infrared sources, heating jackets (either electrical or with a heating fluid), lamps, etcetera. Because of its

simplicity, this process is particularly suitable to be carried out in a continuous mode.

5 Aging may be conducted hydrothermally. Within the context of this description hydrothermal means in the presence of water (or steam) at a temperature above 100°C at elevated pressure, e.g. autogenous pressure. This hydrothermal treatment is particularly advantageous, because this is faster and a higher conversion is obtained. There is no need to wash or filter the product, as unwanted ions (e.g. sodium, chloride, sulphate, phosphate) are absent in the  
10 product.

In a further embodiment of the invention, the process is conducted in a multi-step process, e.g. a slurry of aluminium source and magnesium carboxylate is aged thermally in a first reactor at a mild temperature, followed by a  
15 hydrothermal treatment in a second reactor or vice versa. If desired a preformed QCC may be added to the reactor. Said preformed QCC may be recycled QCC from the reaction mixture or a QCC made separately by the process according to the invention or any other process.

20 The reaction is conducted under acidic conditions, i.e. a pH in the range of 3.5 to 6.5. For the preparation of magnesium-aluminium acetates the preferred range is 5.0 to 6.0; when the carboxylate is formate the preferred range is 4.5 to 6.0. The pH is controlled by addition of acids or bases. These may be fed to the reactor or added to either the magnesium solution and/or the aluminium source  
25 before they are fed to the reactor. An example of a preferred pH modifier is an ammonium base. A preferred acid is a carboxylic acid. By using these acids or bases, no washing step is required to remove deleterious cations.

The Mg/Al molar ratio of the starting compounds is 0.5–5.0, preferably 0.75–5.0.  
30

The degree to which a magnesium carboxylate will react with the aluminium source depends on the nature of the carboxylate anion and on the nature of the aluminium source. In general, acetate is more reactive than formate. Active aluminas, as represented by amorphous aluminium hydroxide gel powders, are  
5 more reactive than transition aluminas, such as pseudo-boehmite. The extent of the reaction depends further on the reaction conditions. For instance, hydrothermal treatments greatly facilitate the reaction. Those skilled in the art will therefore understand that the compositions obtained from the process according to the invention can be complex mixtures containing both QCC and  
10 unreacted (i.e. not reacted to QCC) reagent phases.

The QCCs according to the present invention exhibit broad powder X-ray diffraction (PXRD) patterns that are distinguishable from pure carboxylate salts of magnesium and aluminium. The PXRD patterns of QCCs are also  
15 distinguishable from those of anionic clays and Al-Mg solid solutions. The strongest peak in the pattern occurs in the low 2-theta region corresponding to a basal spacing in the range of 5.0 to 15.0 Å, depending on the ratio of magnesium to aluminium used to prepare the compositions. In the absence of obscuring peaks (see below) two additional broad, but weaker reflections can  
20 be observed at basal spacings in the ranges 3.5-3.7 Å and 2.25-2.35 Å. On the basis of the broadness and limited number of diffraction lines contained in the PXRD-patterns, the magnesium-aluminium carboxylate compositions of the present invention are referred to as quasi-crystalline.

25 Depending on the aluminium reagent used to form the QCCs according to the invention, the weak PXRD reflections of the QCCs may be obscured by reflections of an unreacted alumina phase, so that only the strongest reflection may be observed.

The structure of the QCC and, therefore, the position of its PXRD reflection depends in part on the type of carboxylate, the aluminium source used and the water content of the QCC.

For instance, magnesium-aluminium acetates dried at 120°C show their  
5 strongest reflection in the range of 9.0 to 15.0 Å, whereas magnesium-aluminium formates dried at the same temperature exhibit the corresponding peak in the range of 5.0 to 9.0 Å.

A more reactive (amorphous) alumina gives a quasi-crystalline acetate with a basal spacing near 14 Å, whereas a less reactive alumina, such as pseudo-  
10 boehmite, affords a quasi-crystalline acetate with a spacing near 9.5 Å.

This difference is attributed to a difference in the resulting Mg/Al ratio in the QCC.

The temperature used to dry the QCC also affects the PXRD pattern, because removal of water from the crystal lowers the d-spacing.

15 The QCCs according to the invention can advantageously be used for various purposes which need a reactive Mg/Al reagent or a mild base. For example, QCCs can be used as pharmaceutical anti-acids. Other examples of such applications are the use as absorbent for the purification of waste water or  
20 gaseous streams, as catalyst additive or matrix.

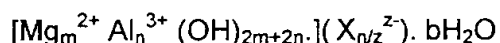
The QCCs according to the invention may be used directly in oven-dried or spray-dried form for the adsorption of SO<sub>x</sub>/NO<sub>x</sub> in the regenerator unit of a FCC process. At the temperature of the regenerator, typically 700°-800°C, the QCCs  
25 according to the invention are transformed into a mixture of metal oxides.

In certain applications, it may be desirable to calcine the QCCs of the present invention in order to remove carboxylate. The QCCs may be converted to magnesium-aluminium oxide compositions by calcination at temperatures in the range of 300° to 1200°C, preferably 400°-1000°C. The calcination may for  
30 instance be carried out in a rotary kiln. Alternatively, the QCC may be flash calcined. The preferred range for removing acetate and formate is 700°-800°C.

Calcination at 700°-800°C of QCCs with Mg/Al ratios in the range 0.5-0.75 leads to products which consist primarily of spinel. As the Mg/Al ratio is increased beyond 0.75, the calcined products comprise, in addition to spinel, magnesium oxide and magnesium-aluminium oxide solid solutions with a  
 5 magnesium oxide lattice structure. This invention therefore relates also to the preparation of Mg-Al solid solutions by calcination of QCCs.

The magnesium oxide and the solid solution phase can be distinguished by rehydration of the calcined product in aqueous suspension. The magnesium  
 10 oxide component reacts very slowly with water to form brucite, i.e. Mg(OH)<sub>2</sub>. In contrast, rehydration of the solid solution results in the formation of an anionic clay within 24 hours. Within this period, magnesium oxide remains largely unreacted.

15 Therefore, this invention also relates to a process for the preparation of anionic clays from QCCs. The anionic clays formed by this method have a layered structure corresponding to the general formula:



20

wherein m and n have a value such that m/n=1 to 10, preferably 1 to 6, and b has a value in the range from 0 to 10, generally a value of 2 to 6 and often a value of about 4. X may be CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup> or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a  
 25 value of 2 to 4, more particularly a value close to 3. If the reaction mixture is free of atmospheric carbon dioxide the product formed by rehydration of the solid solution is a meixnerite-like anionic clay. The PXRD patterns of the rehydrated calcined QCCs according to the invention comprise peaks characteristic of anionic clays with basal spacings in the range 7.0-9.5 Å,  
 30 depending on the Mg/Al ratio and the degree of hydration. Beside these peaks, the rehydrated samples may also comprise peaks indicative for alumina (e.g.

pseudo-boehmite), spinel, unreacted magnesium oxide and/or brucite.

The rehydration to form anionic clays can be performed by contacting the material in water for 1-24 hours at 65°-85°C. Preferably, the slurry is stirred and  
5 has a solids content ranging from 1-50 wt%. During this treatment additives can be added.

If desired, the anionic clay may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing anions are replaced with other  
10 anions. Examples of suitable anions are carbonates, bicarbonates, nitrates, chlorides, sulphates, bisulphates, vanadates, tungstates, borates, phosphates, and pillaring anions such as  $V_2O_7^{4-}$ ,  $HV_2O_{12}^{4-}$ ,  $V_3O_9^{3-}$ ,  $V_{10}O_{28}^{6-}$ ,  $Mo_7O_{24}^{6-}$ ,  $PW_{12}O_{40}^{3-}$ ,  $B(OH)_4^-$ ,  $B_4O_5(OH)_4^{2-}$ ,  $[B_3O_3(OH)_4]^-$ ,  $[B_3O_3(OH)_5]^{2-}$ ,  $HBO_4^{2-}$ ,  $HGaO_3^{2-}$ ,  $CrO_4^{2-}$ , Keggin-ions, formates, acetate and mixtures thereof. Said ion-exchange  
15 can be conducted before or after drying the anionic clay formed by rehydration.

For some applications it is desirable to have additives, both metal compounds and non-metal compounds, comprising rare earth metals (for example Ce, La), Si, P, B, group VI, group VIII, alkaline earth (for instance Ca and Ba) and/or  
20 transition metals (for example W, V, Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn), present in the compositions according to the invention, i.e. the QCCs, the calcined products or the rehydrated products. Said additives can easily be deposited on the compositions or they can be added either to the magnesium carboxylate starting material or the aluminium source before adding to the reactor or they  
25 can be added to the reactor separately. Suitable sources of metal compounds or non-metal compounds are oxides, halides or any other salt such as chlorides, nitrates etcetera.

The compositions according to the invention, i.e. the QCC, the calcined product  
30 or the rehydrated product, may optionally be spray dried to form microspheres, extruded or beaded to form shaped bodies. This shaping can be performed

after, before or, in the case of a multi-step process, during the aging step. If unreacted alumina is present in the composition, i.e. the QCC, the calcined product or the rehydrated product, it acts as a binder.

- 5 Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the slurry used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the
- 10 liquid used in the slurry and/or add an additional or another liquid, and/or change the pH of the precursor mixture to make the slurry gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping.

15

- The incorporation of an  $\text{SO}_x/\text{NO}_x$  absorbant into a FCC process for petroleum refining can be facilitated by combining the absorbant as part of the FCC catalyst particle. The present invention hence also relates to a FCC catalyst comprising a quasi-crystalline magnesium-aluminium carboxylate according to
- 20 the present invention, its calcined form and/or its rehydrated form.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- Figure 1 shows the PXRD patterns of a QCC with a Mg/Al ratio of 0.5, its
- 25 calcined and its subsequently rehydrated form. The alumina source is a peptisable pseudo-boehmite; the carboxylate is acetate.

- Figure 2 shows the PXRD patterns of a QCC with a Mg/Al ratio of 2.0, its calcined and its subsequently rehydrated form. The alumina source is a
- 30 peptisable pseudo-boehmite; the carboxylate is acetate.

Figure 3 shows the PXRD patterns of a QCC with a Mg/Al ratio of 3.0, its calcined and its subsequently rehydrated form. The alumina source is an aluminium hydroxide gel powder; the carboxylate is acetate.

- 5 In these figures QCC stands for quasi-crystalline magnesium-aluminium carboxylate, SP for spinel, Mg/AlO for magnesium-aluminium solid solution, HT for anionic clay and Bo for pseudo-boehmite.
- 10 The instant QCC compositions can also be described as magnesium-aluminium carboxylate compositions comprising a hydrated magnesium hydroxy carboxylate, a hydrated aluminium hydroxy carboxylate, a mixed hydrated magnesium-aluminium hydroxy carboxylate and an aluminium oxide.



## EXAMPLES

Example 1

- 5 A magnesium acetate solution was prepared in this example. Glacial acetic acid (996 g) was added to de-ionised water (1108 g). To this solution 335 g MgO (Spectrum Chemical Company; Hoavy USP powder; MA125) was slowly added, while stirring, until all of the MgO had dissolved producing a solution with pH 5.45.

10

Example 2

- An alumina sol was prepared by adding 50.0 g of Catapal A® alumina (a peptisable pseudo-boehmite produced by the Vista Chemical Company) to a mixture of 3.45 g glacial acetic acid and 245.0 g de-ionised water and mixing in a Waring blender at high speed for 15 minutes. To the resulting mixture, 103.4 g of the magnesium acetate solution of Example 1 was added. The resulting mixture was mixed in the blender for 20 minutes, producing a gel with a pH of 5.53 and a Mg/Al molar ratio of 0.5. The gel was aged at 80°C for 27 hours in a sealed container. The product was dried overnight in an oven at 100°C and ground to fine powder.

- Figure 1 shows the PXRD pattern of the sample. This pattern contains reflections characteristic for unreacted pseudo-boehmite and two reflections of the QCC at about 9° and 24° two theta. A reflection of the pseudo-boehmite phase obscures the third QCC reflection near 38° two theta. Figure 1 also shows the PXRD pattern of this sample after calcination at 732°C and after a subsequent rehydration. These patterns indicate that spinel is the main phase formed. As already mentioned in the description, the spinel phase is not rehydrated to anionic clay.

### Example 3

Example 2 was repeated, except that 413.5 g of magnesium acetate solution was used, resulting in a Mg/Al molar ratio of 2.0. The pH of the gel was 5.45.

- 5 Figure 2 shows the PXRD pattern of the product. The diffraction pattern indicates the formation of QCC and pseudo-boehmite. Figure 2 also shows the PXRD pattern of this sample after calcination at 732°C and a subsequent rehydration. These patterns indicate that after calcination both spinel and Mg/Al solid solution are present. Upon rehydration of this calcined material, the solid  
10 solution is transformed into anionic clay, brucite and magnesium oxide.

### Example 4

- An alumina sol was prepared by adding 30.0 g of Catapal A® alumina (a  
15 peptisable pseudo-boehmite produced by the Vista Chemical Company) to a mixture of 1.99 g glacial acetic acid and 147.0 g de-ionised water and mixing in a Waring blender at high speed for 15 minutes. To the resulting mixture, 496.2 g of the magnesium acetate solution of Example 1 was added. The resulting mixture was mixed in the blender for 20 minutes, producing a gel with a pH of  
20 5.47 and a Mg/Al molar ratio of 4.0.

Three portions of the gel were aged under the following conditions:

- Portion 1. room temperature for 29 hours  
Portion 2. 80°C for 27 hours in a sealed container  
25 Portion 3. 175°C at  $8.2 \cdot 10^5$  Pa (120 psig) for 60 minutes, using a Microwave Sample Preparation System manufactured by the CEM Corporation.

- For all these samples the PXRD diffraction patterns indicated the formation of  
30 QCC and pseudo-boehmite.

Example 5

A dispersion of alumina was prepared by adding 66.8 g of an aluminium hydroxide gel powder (an amorphous alumina produced by the Chattem  
5 Chemicals, Inc.) to a mixture of 3.32 g glacial acetic acid and 108.9 g de-ionised water and mixing in a Waring blender at high speed for 15 minutes. To the resulting mixture, 206.8 g of the magnesium acetate solution of Example 1 was added. The resulting mixture was mixed in the blender for 20 minutes, producing a gel with a pH of 5.75 and a Mg/Al molar ratio of 1.0.  
10 Three portions of the gel were aged under the following conditions:

- Portion 1. room temperature for 29 hours
- Portion 2. 80°C for 27 hours in a sealed container
- Portion 3. 175°C at  $8.2 \cdot 10^5$  Pa (120 psig) for 60 minutes, using a Microwave  
15 Sample Preparation System manufactured by the CEM Corporation.

The samples were dried overnight in an oven at 100°C, ground to fine powder. For the aging carried out at room temperature (Portion 1), the three lines  
20 characteristic of the QCC phase were clearly visible, because the unreacted fraction of the alumina source is amorphous and could not obscure these reflections.

Figure 3 shows the PXRD pattern of the sample aged at 80°C (Portion 2). The diffraction pattern shows the three characteristic QCC reflections. Figure 3 also  
25 shows the PXRD patterns of this sample after calcination at 732°C and a subsequent rehydration. These patterns indicate that after calcination both spinel and Mg/Al solid solution are present. The spinel/solid solution ratio is higher than in Example 3 (Figure 2). Upon rehydration of the calcined material, the majority of the solid solution is transformed into anionic clay and magnesium  
30 oxide.

Similar results were obtained for the sample treated at 175°C.

### Example 6

A dispersion of alumina was prepared by adding 52.5 g of an Versal-250® alumina (a non-peptisable pseudo-boehmite produced by the LaRoche Chemical Company) to a mixture of 3.32 g glacial acetic acid and 123.1 g de-ionised water and mixing in a Waring blender at high speed for 15 minutes. To the resulting mixture, 206.8 g of the magnesium acetate solution of Example 1 was added. The resulting mixture was mixed in the blender for 20 minutes, producing a gel with a pH of 5.67 and a Mg/Al molar ratio of 1.0.

Three portions of the gel were aged under the following conditions:

- Portion 1. room temperature for 29 hours
- Portion 2. 80°C for 27 hours in a sealed container
- 15 Portion 3. 175°C at  $8.2 \cdot 10^5$  Pa (120 psig) for 60 minutes, using a Microwave Sample Preparation System manufactured by the CEM Corporation.

In all cases, the PXRD patterns showed the formation of QCC and pseudo-boehmite.

### Example 7

An alumina sol was prepared by adding 40.0 g of Catapal A ® alumina (a peptisable pseudo-boehmite produced by the Vista Chemical Company) to a mixture of 3.25 g formic acid (8 wt.%) and 148.0 g de-ionised water and mixing in a Waring blender at high speed for 15 minutes. To the resulting mixture, a solution of 81.8 g of magnesium formate (Pfaltz & Bauer, Co) dissolved in 463.0 g de-ionised water was added. The resulting mixture was mixed in the blender for 20 minutes, producing a gel with a pH of 5.53 and a Mg/Al molar ratio of 1.0. The gel was aged at 80°C for 48 hours in a sealed container. The product was

dried overnight in an oven at 100°C and ground to fine powder. The PXRD diffraction pattern indicated the formation of QCC and pseudo-boehmite.

#### Example 8

5

An aqueous solution of magnesium acetate was mixed with an aqueous solution of quantitative amounts of aluminium nitrate. Samples with different Mg/Al ratios (in the range 0.5-5.0) were aged at room temperature for 27 hours and the pH was adjusted to 6.0 by using ammonium hydroxide. The resulting  
10 precipitates were collected by filtration and oven-dried. PXRD indicated the formation of QCC in all these samples.

## CLAIMS:

(44)

1. A composition comprising a quasi-crystalline hydrated magnesium-aluminium hydroxy carboxylate, with at least a reflection in the powder X-ray  
5 diffraction pattern in the range of 5 to 15 Å.
2. A composition according to claim 1, also comprising a hydrated magnesium hydroxy carboxylate and/or a hydrated aluminium hydroxy carboxylate.
- 10 3. A composition according to claim 1 or 2, also comprising an aluminium oxide.
4. A composition according to any one of the previous claims, characterised in that the carboxylate is acetate or formate.
- 15 5. A compositions according to any one of the previous claims, characterised in that the magnesium to aluminium molar ratio in the composition ranges from 0.5 to 5.0.
- 20 6. A composition according to claim 5, characterised in that the magnesium to aluminium molar ratio in the composition ranges from 0.75 to 5.0.
7. Process for the preparation of a composition according to any one of the previous claims, characterised in that a mixture of an aluminium source and  
25 a magnesium carboxylate is aged at a pH ranging from 3.5 to 6.5.
8. Process according to claim 7, characterised in that the magnesium carboxylate is magnesium acetate or magnesium formate.

9. Process according to claim 7 or 8, characterised in that the aluminium source is an aluminium salt, pseudo-boehmite, amorphous aluminium hydroxide gel powder, or a mixture thereof.
- 5 10. Process according to any one of the claims 7-9, characterised in that the mixture is aged at hydrothermal conditions.
11. Process according to any one of the claims 7-10, characterised in that the process is conducted in two separate steps, one under thermal and one  
10 under hydrothermal conditions.
12. Process according to any one of the claims 7-11, characterised in that the process is conducted in a continuous mode.
- 15 13. Process according to any one of the claims 7-12, characterised in that the composition is shaped.
14. Process for the preparation of Mg-Al solid solutions, characterised in that a composition according to any one of the claims 1-6 is calcined at  
20 temperatures in the range of 300° to 1200°C.
15. Process for the production of an anionic clay, characterised in that a composition according to any one of the claims 1-6 is calcined and subsequently rehydrated to obtain an anionic clay.
- 25 16. Mg-Al solid solution obtainable by the process according to claim 14.
17. Anionic clay obtainable by the process according to claim 15.
- 30 18. Catalyst composition comprising a composition according to any one of the claims 1-6.

05 03. 2001

## ABSTRACT

(44)

5 The present invention provides new compositions of matter, referred to as quasi-crystalline carboxylates (QCCs), their preparation and use. These materials comprise a quasi-crystalline hydrated magnesium-aluminium hydroxy carboxylate and are characterised by the presence of at least a strong reflection in the powder X-ray diffraction pattern at a basal spacing in the range of 5 to 15 Å.

10

The invention further relates to a process for preparing QCCs, Mg-Al solid solutions and anionic clays under acidic conditions. The method comprises aging of an acidic mixture of a magnesium carboxylate and an aluminium source, resulting in a QCC. Calcination of this composition results in a Mg-Al solid solution; rehydration of this solid solution gives an anionic clay.

20



Figure 1

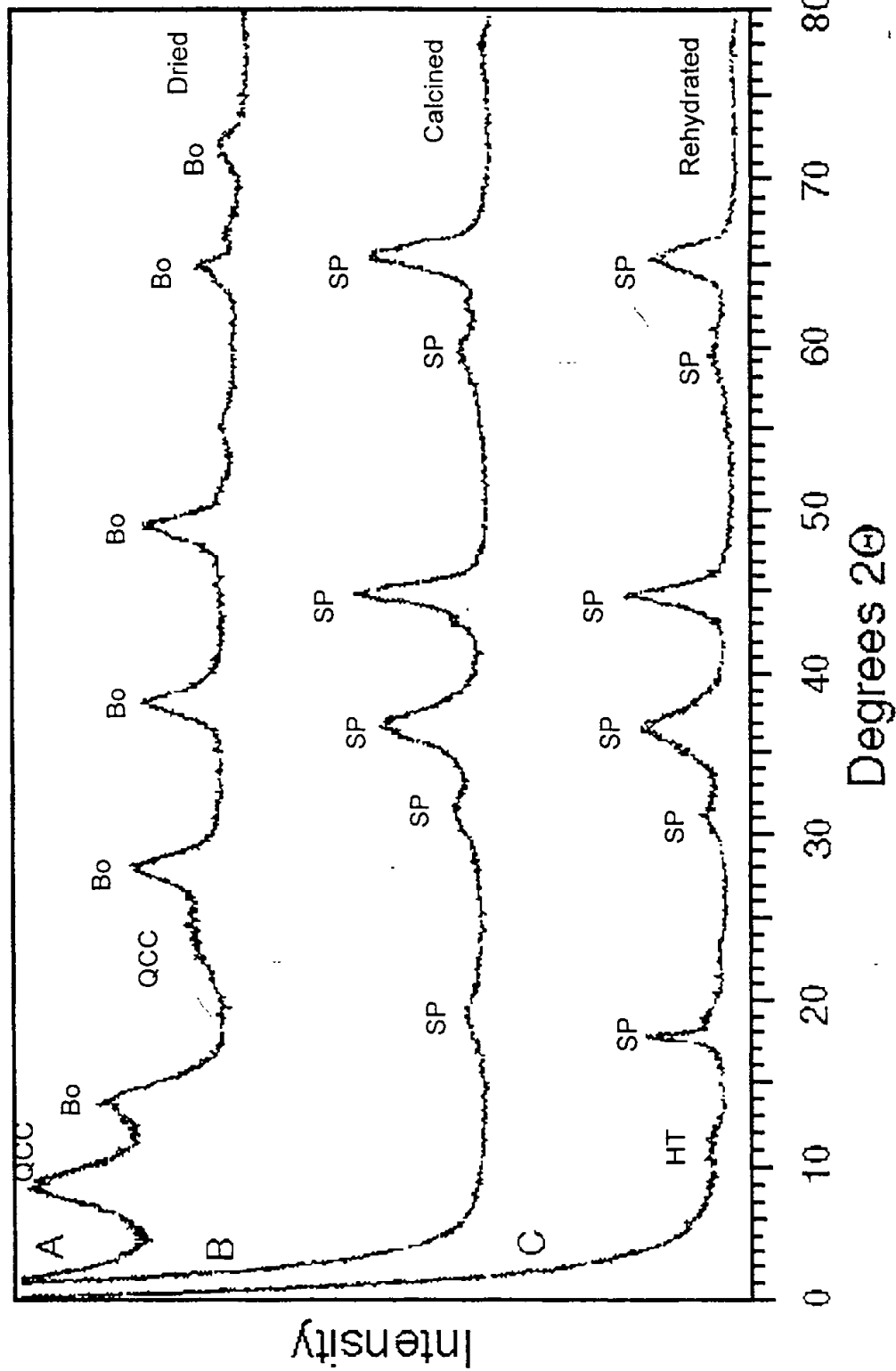


Figure 2

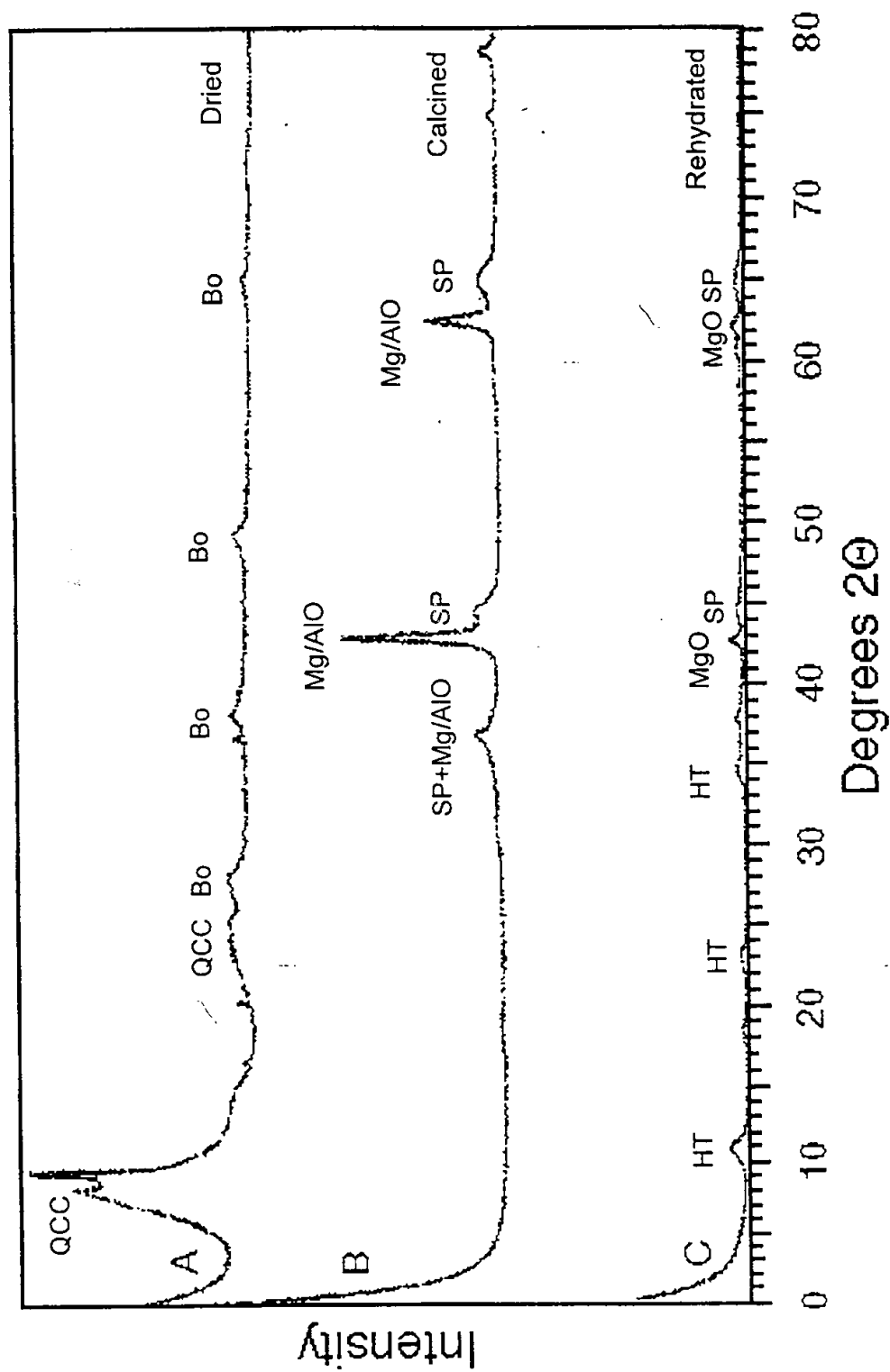


Figure 3

